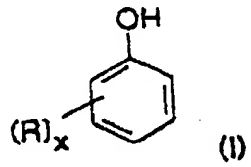
CLAIMS

1 - A process for the preparation of optionally substituted p-hydroxymandelic compounds and derivatives, which consists in carrying out the condensation, in water, in the presence of an alkaline agent, of an aromatic carrier compound with at least one hydroxyl group and the para position of which is free, with glyoxylic acid, said process being characterised in that the reaction is carried out in the presence of an effective quantity of a carrier compound with at least two carboxylic functions.

2 - A process according to claim 1, ~~characterised in that~~ the hydroxylated compound corresponds to the following formula (I):



(I)

in which formula (I):

- the para position is free,
- x is an integer between 1 and 4,
- R represents :
  - a hydrogen atom,
  - a hydrocarbon group having from 1 to 20 carbon atoms selected from the alkyl, alkoxy, hydroxyalkyl, cycloalkyl, aryl, phenoxy, alkoxyalkyl, fluoroalkyl, hydroxyalkoxyalkylene groups,
  - a hydroxyl group,
  - a –CHO group,
  - an acyl group having from 2 to 6 carbon atoms,
  - a halogen atom, ~~preferably a fluorine, chlorine or bromine atom~~,
  - two R groups placed on two vicinal carbon atoms can form together and with the carbon atoms which carry them a benzene ring.

3 - A process according to ~~either claim 1 or claim 2,~~ ~~characterised in that~~ the hydroxylated aromatic compound corresponds to formula (I), in which:

- x is equal to 0, 1, 2 or 3,

- R represents one of the following groups or functions:

. a hydrogen atom,

. a linear or branched alkyl radical having from 1 to 10 carbon atoms, ~~and preferably from 1 to 4 carbon atoms,~~

. a linear or branched alkoxy radical having from 1 to 10 carbon atoms, ~~preferably from 1 to 4 carbon atoms,~~

. an -OH group,

. a –CHO group,

. a halogen atom,

. a $-CF_3$ group.

4 - A process according to ~~one of claims 1 to 3, characterised in that~~ claim 27 wherein the hydroxylated aromatic compound corresponds to formula (I) in which the R radicals which are identical or different are a hydrogen atom, a linear or branched alkyl radical with 1 to 4 carbon atoms, a linear or branched alkoxy radical with 1 to 4 carbon atoms, a -CHO group, a chlorine atom, and x is ~~preferably~~ equal to 0 or 1.

5 - A process ~~according to one of claims 1 to 4, characterised in that~~ claim 27 wherein the hydroxylated aromatic compound of formula (I) is ~~phenol,~~ o-cresol, m-cresol, 3-ethyl phenol, 2-tert-butyl phenol, guaiacol, guetol, and 2-isopropoxy phenol.

6 - A process according to ~~one of claims 1 to 5, characterised in that~~ claim 27 wherein the catalyst is a compound carrying at least two carboxylic functions corresponding to the following formula (II):

$HOOC-R_1-COOH$ (II)

in which formula (II), R_1 represents a valency bond or an optionally substituted hydrocarbon radical containing 1 to 40 carbon atoms.

7 - ~~A process according to claim 6, characterised in that~~ wherein the catalyst is a carrier compound having at least two carboxylic functions corresponding to formula (II) wherein R_1 symbolises a substituted or non-substituted hydrocarbon radical which can be a linear or branched, saturated or unsaturated acyclic aliphatic radical; a monocyclic or polycyclic,

saturated, unsaturated, or aromatic carbocyclic radical; a monocyclic or polycyclic, saturated, unsaturated or aromatic heterocyclic radical.

8 - A process according to claim 6, ~~characterised in that~~ wherein the catalyst is a carrier compound with at least two carboxylic functions corresponding to formula (II), in which R_1 represents a linear or branched, acyclic aliphatic residue having ~~preferably~~ 1 to 12 carbon atoms, saturated or containing one or more unsaturations on the chain, ~~generally 1 to 3 unsaturations~~ which can be single or conjugated double bonds, or triple bonds; the hydrocarbon chain can optionally be:

(1) - interrupted by one of the following groups called Y:

$$-O-;\ -CO-;\ -COO-;\ -\underset{\underset{R_2}{|}}{N}-;\ -CO-\underset{\underset{R_2}{|}}{N};\ -S-;\ -SO_2-$$

in which formulae R_2 represents hydrogen or a linear or branched alkyl radical having 1 to 4 carbon atoms, or a radical of $-(CH_2)_p - COOH$ type in which p is a number between 1 and 5,

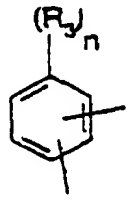
(2) - and/or bearing one of the following substituents:

$-OH;\ -COOH;\ -CHO;\ -NO_2;\ -CN;\ -NH_2;\ -SH;\ -X;\ CF_3$

$-NH-[(CH_2)_p-COOH]$ or $-N-[(CH_2)_p-COOH]_2$

with X representing a halogen atom, ~~preferably a fluorine, chlorine or bromine atom~~, and p having the meaning given hereinabove.

9 – A process according to claim 6, ~~characterised in that~~ wherein the catalyst is a carrier compound with at least two carboxylic functions corresponding to formula (II), in which R_1 represents an ~~aromatic hydrocarbon residue, and, in particular,~~ a benzene residue corresponding to the general formula (III):



(III)

in which formula (III):

- n is an integer from 0 to 4, ~~preferably from 0 to 2,~~
- R_3 represents one of the following groups or functions,

. a hydrogen atom,
. a linear or branched alkyl radical having from 1 to 4 carbon atoms,
. a linear or branched alkoxy radical having from 1 to 4 carbon atoms,
. a methylene or ethylene dioxy radical,
. a –CHO group,
. a phenyl or benzyl radical,
. a halogen atom.

10 - A process according to claim 6, ~~characterised in that~~ wherein the catalyst is a carrier compound with at least two carboxylic functions corresponding to formula (II) in which the R_1 radical represents a polycyclic aromatic hydrocarbon divalent residue; the rings can form between themselves ortho-condensed, ortho- and peri-condensed systems.

11 - A process according to claim 6, ~~characterised in that~~ wherein the catalyst is a carrier compound with at least two carboxylic functions corresponding to formula (II), in which R_1 represents a carbocyclic residue which is saturated or contains 1 or 2 unsaturations in the ring, ~~generally having 3 to 7 carbon atoms, preferably 6 carbon atoms, in the ring~~.

12 - A process according to ~~one of claims 6 to 11,~~ claim 6 wherein ~~characterised in that~~ the catalyst is a carrier compound with at least two carboxylic functions corresponding to formula (II), in which R_1 represents a divalent radical constituted by a chain formation of two to four residues as defined hereinabove, an aliphatic residue, an aromatic residue or a cycloaliphatic residue, connected together by a valency bond or by a function group.

13 - A process according to claim 6, characterised in that the catalyst is a carrier compound with at least two carboxylic functions corresponding to formula (II) selected from:

- dicarboxylic aliphatic acids, such as:
. oxalic acid
. malonic acid
. succinic acid
. glutaric acid
. adipic acid
. 2,4-dimethyl adipic acid
. pimelic acid

. suberic acid
. azelaic acid
. sebacic acid
. dodecane dioic acid
. fumaric acid
. maleic acid

- cycloalkanedicarboxylic acids, such as cyclohexane 1,4-dicarboxylic acid,
- aromatic dicarboxylic acids, such as:
  . phthalic acid
  . isophthalic acid
  . terephthalic acid
  . phenylenediacetic acid
  . naphthalene 1,5-dicarboxylic acid
  . naphthalene 1,6-dicarboxylic acid
  . 4,4'-diphenylcarboxylic acid
  . 3,3'-diphenylcarboxylic acid
  . bis(4-hydroxycarbonyl) phenyl oxide
  . bis(3-hydroxycarbonyl) phenyl oxide
  . 4,4'-dihydroxycarbonyl diphenylsulphone
  . 3,3'-dihydroxycarbonyl diphenylsulphone
- pyrimidine or imidazole dicarboxylic acids.
- aminopolycarboxylic acids:
  . ethylenediaminotetracetic acid (E.D.T.A.)
  . diethylenetriaminopentacetic acid (D.T.P.A.)
  . nitrilotriacetic acid (N.T.A.)
  . N-(2-hydroxyethyl)ethylene diaminotriacetic acid (H.E.D.T.A.).

14 - A process according to ~~one of claims 1 to 13, characterised in that~~ claim 27 wherein the aqueous solution of glyoxylic acid contains monofunctional acids~~, in particular from 0.1 to 3% acetic acid~~.

15 - A process according to ~~one of claims 1 to 14, characterised in that~~ claim 27 wherein the aqueous solution of glyoxylic acid has a concentration which varies from 15 to 70% by weight~~, preferably in the region of 50% by weight~~.

16 - A process according to ~~one of claims 1 to 15~~ claim 27 wherein, ~~characterised in that~~ the molar ratio between the hydroxylated aromatic compound of formula (I) and the glyoxylic acid varies between 1.5 and 4.0 ~~and is preferably selected between 2.0 and 3.0~~.

17 - A process according to ~~one of claims 1 to 16~~ claim 27 wherein, ~~characterised in that~~ the quantity of alkali metal hydroxide is in the region of, or equal to, the stoichiometric quantity necessary to salify all the salifiable groups of the hydroxylated aromatic compound of formula (I) and to salify the carboxylic function of the glyoxylic acid.

18 - A process according to ~~one of claims 1 to 17~~ claim 27 wherein, ~~characterised in that~~ the concentration of the hydroxylated aromatic compound of formula (I) is ~~preferably comprised~~ between 0.5 and 1.5 moles/litre~~, and more particularly in the region of 1 mole/litre~~.

19 - A process according to ~~one of claims 1 to 18~~ claim 27 wherein, ~~characterised in that~~ the quantity of catalyst used is such that the molar ratio between the catalyst and the hydroxylated aromatic compound of formula (I) is between 0.005 and 0.025 ~~and preferably between 0.01 and 0.02~~.

20 - A process according to ~~one of claims 1 to 19~~ claim 27 wherein, ~~characterised in that~~ the quantity of catalyst used, as expressed by the ratio between the number of moles of catalyst and the number of moles of glyoxylic acid, is selected between 0.5 and 2.5% ~~, preferably between 1 and 2%~~.

21 - A process according to ~~one of claims 1 to 20~~ claim 27 wherein, ~~characterised in that~~ the catalyst is entirely or partly provided by the aqueous solution of glyoxylic acid.

22 - A process according to claim 21 wherein, ~~characterised in that~~ the solution of glyoxylic acid comprises between 0.6 and 3% ~~, preferably between 1.2 and 2.6%~~ by weight, of oxalic acid, as expressed in relation to the weight of glyoxylic acid.

23 - A process according to ~~one of claims 1 to 22, characterised in that~~ claim 27 wherein the catalyst is introduced with the aqueous solution of glyoxylic acid or into the starting reaction medium containing the hydroxylated aromatic compound of formula (I), water and the alkali metal hydroxide.

24 - A process according to ~~one of claims 1 to 23~~, ~~characterised in that~~ the temperature of the reaction varies between 20°C and 60°C ~~(preferably between 30°C and 40°C.~~

25 - Use of the optionally substituted p-hydroxymandelic compounds obtained according to one of claims 1 to 24 as intermediates for the production of hydroxyarylacetic acids, hydroxyarylglyoxylic acids, or hydroxyaromatic aldehydes.

26 - Use of p-hydroxymandelic acid and 3-methoxy p-hydroxymandelic, 3-ethoxy p-hydroxymandelic acids or 3-isopropoxy p-hydroxymandelic acids obtained in accordance with the preparation process described in ~~one~~ of claims 1 to 24 for the production of 4-hydroxy benzaldehyde and vanillin and analogues by oxidation of said acids.